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Experimental Determination of the Coefficient  
in the Steady State Current Equation for Spherical Segment Microelectrodes

by

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EXPERIMENTAL DETERMINATION OF THE COEFFICIENT IN THE STEADY  
STATE CURRENT EQUATION FOR SPHERICAL SEGMENT  
MICROELECTRODES

by

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# ABSTRACT

The coefficient in the steady state current equation for spherical segment microelectrodes has been evaluated experimentally for various values of the height of the spherical segment. For this purpose chronoamperometric reduction of  $\text{Hg}_2^{+2}$  ion at a silver microdisc electrode in perchloric acid solution has been employed. The diffusion coefficient of  $\text{Hg}_2^{+2}$  in 0.25 M  $\text{HClO}_4$  at 30° C was determined as  $1.12 \times 10^{-5} \text{ cm}^2/\text{s}$ .



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A variety of shapes of microelectrodes (i.e., electrode with at least one dimension in the micrometer range) have been examined and characterized as reported in the literature so far. This includes discs, rings, cylinders, lines and hemispheres (1). Usually microelectrodes are made from metals or graphitic materials. However, mercury microelectrodes are also needed. Several such microelectrodes have been prepared and applied (2-13).

Application of mercury microelectrodes for voltammetric purposes requires that the mercury surface is coherent and does not consist of isolated droplets. It has been shown that hemispherical mercury electrodes which work well can be prepared by electrodeposition of the predetermined amount of mercury on a platinum microdisc in a separate plating step (4,8,10,13). Iridium has also been proposed as a substrate (9). However, iridium wires thinner than 127  $\mu\text{m}$  are not available commercially. Recently a dropping mercury microelectrode has been constructed. The operation of the device is based on heating a mercury reservoir which drives the droplets through a capillary (14).

In many of these cases the geometry is not well-defined. For example, Wehmeyer and Wightman (4) assume that mercury deposited on platinum substrates is hemispherical. However the deposition current at substrates of different sizes (all other conditions being identical) is about the same, and the radii of the "hemispheres" determined experimentally are in general greater (as much as 24 times) than the radius of the substrate. For this case apparently the mercury most closely resembles a shielded sphere with a point of attachment, and the deposition current increases with time as  $t^{1/2}$ , as expected for growth of a single nucleus.

We are concerned here with a different geometry, that of the spherical segment. This model applies when the metallic substrate is uniformly wet by

mercury, and deposition of mercury increases the height of the segment, but the base (the metallic substrate) remains fixed. The diffusion problem for the intermediate geometry of the spherical segment is complex and has not been solved for the general case. However, there is considerable interest in use of such geometries experimentally. Therefore, the aim of the present paper is to determine experimentally the dependence of the steady-state current on the height of the spherical segment. This has been accomplished by analysis of the chronoamperometric deposition of mercury on an easily-wettable microdisc electrode. The steady-state current thus measured at a given time was directly related to the height of the spherical segment through Faraday's Law, assuming that the volume of mercury is always in the shape of a spherical segment.

A coherent mercury microelectrode obtained by deposition of mercury on a metallic disk substrate (of radius  $r$ ) has the shape of a segment of a sphere (of radius  $R$ ) with altitude  $h$  and one base of radius  $r$ . The volume,  $V$ , and lateral surface area,  $A$ , of such an electrode are (15)

$$V = \pi h(3r^2 + h^2)/6 = \pi h^2[3R-h]/3 \quad (1)$$

$$A = \pi(r^2 + h^2) = 2\pi Rh \quad (2)$$

respectively. The radius of curvature of the lateral surface is

$$R = (h + r^2/h)/2 \quad (3)$$

The steady state current at such an electrode can be described by

$$I_{ss} = knFCDr \quad (4)$$

where  $C$  denotes bulk concentration of the depolarizer and  $D$  is its diffusion coefficient. For a microdisc electrode ( $h = 0$ ),  $k = 4$  (16), and for an ideal hemisphere ( $h = r$ ),  $k = 2\pi$ . The latter can be obtained by applying considerations of symmetry to the well-known equation for a spherical electrode. In some cases it is more convenient to express the steady-state current in terms of electrode area. Then  $i_{ss} = k'nFADC/r$ , where  $k' = 4/\pi$  for a disk and  $k' = 1$  for a hemisphere. The quantity  $k'$  is related to  $k$  (eq 4) by  $k' = k/\pi [1 + (h/r)^2]$ . The situation where  $h$  is not equal to  $r$  complicates the analysis of experimental results, since then the coefficient for the steady state current equation,  $k$ , is not known. However, it is much more convenient to make an electrode of known but arbitrary  $h$  than to be constrained to the hemispherical geometry. The case  $h \approx 0$  is not a practical alternative.

## EXPERIMENTAL SECTION

Chronoamperometric experiments involving electrodeposition of mercury on microdisc electrodes were done on a Micro-g antivibration table produced by Technical Manufacturing Corporation. The instrumental setup consisted of an EG&G PARC model 273 potentiostat in the high speed mode controlled by a MC 68020 Masscomp computer. The cell together with the electrometer probe was kept in a Faraday cage.

Platinum and silver microdisc electrodes of radius  $12.5\text{ }\mu\text{m}$  were employed as the working electrodes. The outer diameter of the insulator was about  $1\text{ mm}$ . Thus ratio of diameters of about 400 should ensure conformity with the model of an electrode embedded in an infinite insulating plane. A saturated calomel electrode (SCE) and a platinum foil served as the reference and auxiliary electrodes respectively. The wires were either sealed into glass capillaries or mounted in low density epoxy resin. Before experiments, the working microelectrodes were polished with alumina powder (the final size was  $0.05\text{ }\mu\text{m}$ ). The electrode shape was examined under a Leitz Diavert microscope.

The electrodeposition of mercury was carried out from  $0.025\text{ M Hg}_2(\text{ClO}_4)_2$  solution in  $0.25\text{ M HClO}_4$ . The reagents were of analytical grade. Deionized water was obtained by passing distilled water through a four cartridge Milli-Q purification system. The solution was degased with argon. To avoid possible convection the gas valve was closed during the current measurement.

Chronoamperometric currents were sampled each  $0.5\text{ s}$  and integrated numerically by means of the trapezoid rule.



## RESULTS

The key point in this experiment is to ensure smooth spreading of the mercury during the electrodeposition process. Usually, at platinum, mercury electrodeposition proceeds through formation of one or a few isolated drops which do not cover the entire surface; the wetting process is slow. As a result the reduction current is higher than it should be for a surface with evenly spread mercury. When the mercury droplets coalesce, a sudden drop in the current should be observed due to decrease in the surface area. We tried to increase the rate of the wetting process by cycling the potential between 0 and +0.8 V in the plating solution. This procedure leads to formation of a thin layer of  $\text{HgPt}_2$ ,  $\text{HgPt}$  and  $\text{Hg}_2\text{Pt}$  compounds (17) and might activate the electrode towards mercury electrodeposition. However, we did not manage to speed up the wetting process sufficiently, and all chronoamperograms obtained at platinum electrodes displayed the sudden drops in current characteristic of coalescence of mercury droplets. This behavior is illustrated in the typical curve obtained with a platinum microelectrode in Figure 1. To avoid this problem we turned to a silver substrate.

Silver is wettable by mercury much more easily than platinum. Its solubility in mercury is 0.086 at % at 28 °C (18). Mercury forms with silver a solid amalgam, but the rate of its formation is slow. For example, a thickness of 1  $\mu\text{m}$  of amalgam can form in about 6.5 hours (19). Also, any formation of the solid amalgam should not lead to shrinking of the mercury hemisphere. Therefore, the possible formation of the solid amalgam on our experimental time scale can be neglected. The final selection of the best silver electrode for the chronoamperometric experiment was done on the basis of the lowest background currents. In this experiment, subtracting a background current is unreasonable since the electrode is changing its

electrochemical nature during the experiment. An acceptable background curve is presented in Figure 2. It is clear that at -0.1 V there is no possibility of hydrogen evolution, and the background current is lower than 1 nA. Still, to enhance the rate of wetting, it was necessary to apply for 0.1 s a prepulse to +0.48 V, where silver is moderately oxidized to  $\text{Ag}^+$ . A curve obtained with a silver microdisc electrode pretreated in this manner is shown in Figure 1. The curve is monotonically increasing with time after the first few seconds and does not display the sharp decreases in current characteristic of coalescence of droplets.

The decrease in current in the first few seconds is the usual transient response to a potential step. The subsequent continuing increase is due to increase in electrode area as mercury is deposited. The resulting minimum current, here  $I = 2.84 \mu\text{A}$  at  $t = 11 \text{ s}$ , should be close to the steady state current. At short times, when the amount of mercury deposited is small, we use the equation for the time-dependent current at a disk:

$$I_{\text{exp}} = I_{\text{ss}} f(\tau) \quad (5)$$

where  $f(\tau) = 1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.0064558\tau^{-5/2}$ ,  $\tau = 4Dt/r^2$ , and  $t$  is time (16). After 11 seconds  $f(\tau) = 1.041$ , which gives for  $I_{\text{ss}}$  the value  $2.73 \mu\text{A}$  and for the diffusion coefficient  $1.13 \times 10^{-5} \text{ cm}^2/\text{s}$ . Diffusion coefficients reported in the literature for  $\text{Hg}_2^{+2}$  in  $\text{HClO}_4$  at  $30^\circ\text{C}$  are 1.05, 1.08, 1.25, and  $1.21 \times 10^{-5} \text{ cm}^2/\text{s}$  in 0.1, 0.5, 1, and 2 M  $\text{HClO}_4$ , respectively, with an error estimated by the authors as 6% (20). Our value fits well in the range of these data.

In fact, at  $t = 11 \text{ s}$ , the amount of charge is  $3.13 \mu\text{C}$ , which corresponds to a height of  $1.947 \mu\text{m}$ . Thus the value of the diffusion

coefficient should be adjusted downward to  $1.12 \times 10^{-5} \text{ cm}^2/\text{s}$ , still well within the range of expected values.

While time in the chronoamperometric experiment elapses, the value of  $f(\tau)$  decreases, reaching the values of 1.029 and 1.0155 at 22 and 77.33 seconds, respectively (assuming constant radius of 12.5  $\mu\text{m}$ ). During this time period the current actually increases, however, due to the increase in surface area. The mercury volume and area of an ideal hemisphere on a 12.5  $\mu\text{m}$  radius silver disc was reached at 77.33 seconds, for which time  $f(\tau)$  calculated for a disc electrode of the same area as the resulting hemisphere is 1.022. This deviation from the steady-state current at a hemispherical electrode can be also calculated from the well-known equation for a sphere

$$I_{\text{sph}}(t) = 4\pi nFDc r [1 + r/(\pi Dt)]^{1/2} = I_{\text{ss}} f(\tau). \quad (6)$$

We assume that the equation for  $f(\tau)$  for the hemisphere is the same, and thus  $f(\tau) = 1.024$  for  $t = 77.33 \text{ s}$  and  $r = 12.5 \mu\text{m}$ .

The ratio of  $\text{Hg}_2^{+2}$  reduction currents after 77.33 and 11 seconds (ideal hemisphere and disc, respectively) is  $0.4429/0.284 = 1.559$ . Applying eq 5 with the values of  $f(\tau)$  above we obtain the ratio 1.580, whereas the theoretical ratio is  $2\pi/4 = 1.5708$ . The difference of only 0.6% is a good test for correctness of the experiment. We have assumed that the current measured at 77.33 is more reliable as a reference point than that at 11 s and have corrected the latter value so that the ratio is 1.5708.

The final results presented in Figure 3 and Table 1 give the coefficient  $k$  as a function of the ratio  $h/r$ . We were not able to find a simple function which yields these values. Because the formula for  $f(\tau)$  is uncertain, the results of Table 1 should not be applied for situations where

$f(r)$  is much different from unity. For  $0 < h < r$ , the accuracy appears to be within about 2%. For  $h > r$  one is extrapolating rather than interpolating, so the treatment is less certain. From eq 3, for  $h=2r$ ,  $R$  is only  $5r/4 \approx r$ , so the shape is still resembles a hemisphere on an insulating plane more than a shielded sphere with a point of attachment. Also the regular behavior of the current-time transient in this region ( $t > 77s$ ) suggests that the extrapolation is reasonable. Special caution should be taken, however, with double potential step experiments for  $h > r$ , because products formed on the forward step might be trapped in the region between the mercury and the insulating substrate. It should be emphasized that the main difficulty is to achieve experimentally the smooth curve of Figure 1b. The smooth curves themselves are quite reproducible. These results should prove useful to the experimentalist and also should guide attempts to solve the corresponding diffusion problem.

CREDIT

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LITERATURE CITED

1. Fleischmann, M.; Pons, S.; Rolison, D.; Schmidt, P.P., Eds. Ultramicro-electrodes: Datatech Science, Morgantown, N.C., 1987.
2. Cushman, M.R.; Anderson, C.W. *Anal. Chim. Acta* 1981, 130, 323.
3. Schulze, G.; Frenzel, W. *Anal. Chim. Acta* 1984, 159, 95.
4. Wehmeyer, K.R.; Wightman, R.M. *Anal. Chem.* 1985, 57, 1989.
5. Ciszowska, M.; Stojek, Z. *J. Electroanal. Chem.* 1985, 191, 101.
6. Baranski, A.S.; Quon, H. *Anal. Chem.* 1986, 58, 407.
7. Golas, J.; Osteryoung, J. *Anal. Chim. Acta* 1986, 181, 211.
8. Howell, J.O.; Kuhr, W.G.; Ensman, R.E.; Wightman, R.M. *J. Electroanal. Chem.* 1986, 209, 77.
9. Golas, J.; Galus, Z.; Osteryoung, J. *Anal. Chem.* 1987, 59, 389.
10. Baranski, A.S. *Anal. Chem.* 1987, 59, 662.
11. Sottery, J.P.; Anderson, C.W. *Anal. Chem.* 1987, 59, 140.
12. Li, L.J.; Fleischmann, M.; Peter, L.M. *Electrochim. Acta* 1987, 32, 1585.
13. Stojek, Z.; Osteryoung, J. *Anal. Chem.* 1988, 60, 131.
14. Pons, J.W.; Daschbach, J.; Pons, S.; Fleischmann, M. *J. Electroanal. Chem.* 1988, 239, 427.
15. *Lange's Handbook of Chemistry*, Dean, J.A., Ed., McGraw Hill: New York, 13th Ed., p 1-13.
16. Aoki, K.; Osteryoung, J. *J. Electroanal. Chem.* 1984, 160, 335.
17. Hassan, M.Z.; Unterecker, D.F.; Bruckenstein, S. *J. Electroanal. Chem.* 1973, 42, 161.
18. Hirayama, C.; Galus, Z.; Guminski, C., Eds. Solubility Data Series, Metals in Mercury, Pergamon Press, London, 1987.
19. Stojek, Z.; Kublik, Z. *J. Electroanal. Chem.* 1975, 60, 349.
20. Levart, E.; d'Angelo d'Orsay, E.P. *J. Electroanal. Chem.* 1966, 12, 277.

FIGURE CAPTIONS

Figure 1: Chronoamperometric reduction curves of  $0.025 \text{ M Hg}_2^{2+}$  in  $0.25 \text{ M HClO}_4$ .  $T = 30 \text{ C}$ : a) platinum, b) silver disc, both  $12.5 \text{ }\mu\text{m}$  in radius.

Figure 2: Cyclic staircase curve obtained with a  $12.5 \text{ }\mu\text{m}$  radius silver disc electrode in  $0.25 \text{ M HClO}_4$ . Step height =  $10 \text{ mV}$ , step width =  $0.1 \text{ s}$ ,  $T = 30 \text{ C}$ .

Figure 3. Coefficient  $k$  plotted vs.  $h/r$  ratio (see Table 1).

TABLE 1.

The coefficient  $k$ , in the steady-state current equation (eq 4) for spherical segment microelectrodes<sup>a</sup>.

$\frac{h}{r}$	$k$	$\frac{h}{r}$	$k$
0	4.0	1.0838	6.670
0.128	4.03	1.1375	6.897
0.2112	4.087	1.2415	7.365
0.2528	4.172	1.2919	7.55
0.2804	4.215	1.3411	7.82
0.3148	4.257	1.4147	8.174
0.349	4.342	1.439	8.316
0.383	4.413	1.533	8.770
0.417	4.484	1.6237	9.224
0.450	4.541	1.712	9.650
0.4836	4.626	1.797	10.10
0.549	4.797	1.880	10.53
0.6136	4.981	1.961	10.94
0.677	5.166	2.040	11.34
0.739	5.378	2.116	11.75
0.800	5.591		
0.859	5.776		
0.917	6.003		
0.974	6.192		
1.0	6.2832		

<sup>a</sup> $h/r$  = height of spherical segment divided by radius of circular substrate.



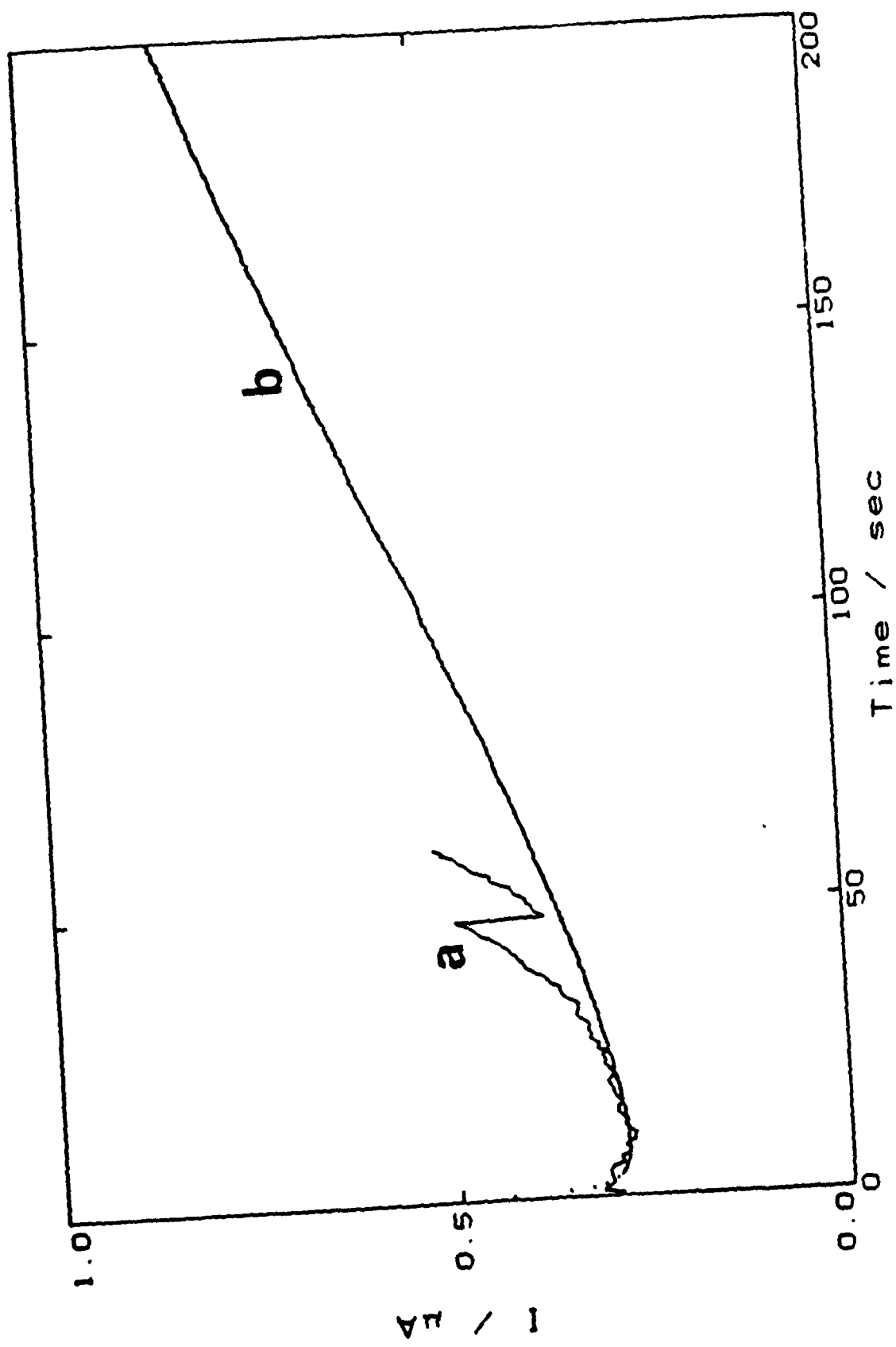


FIGURE 1

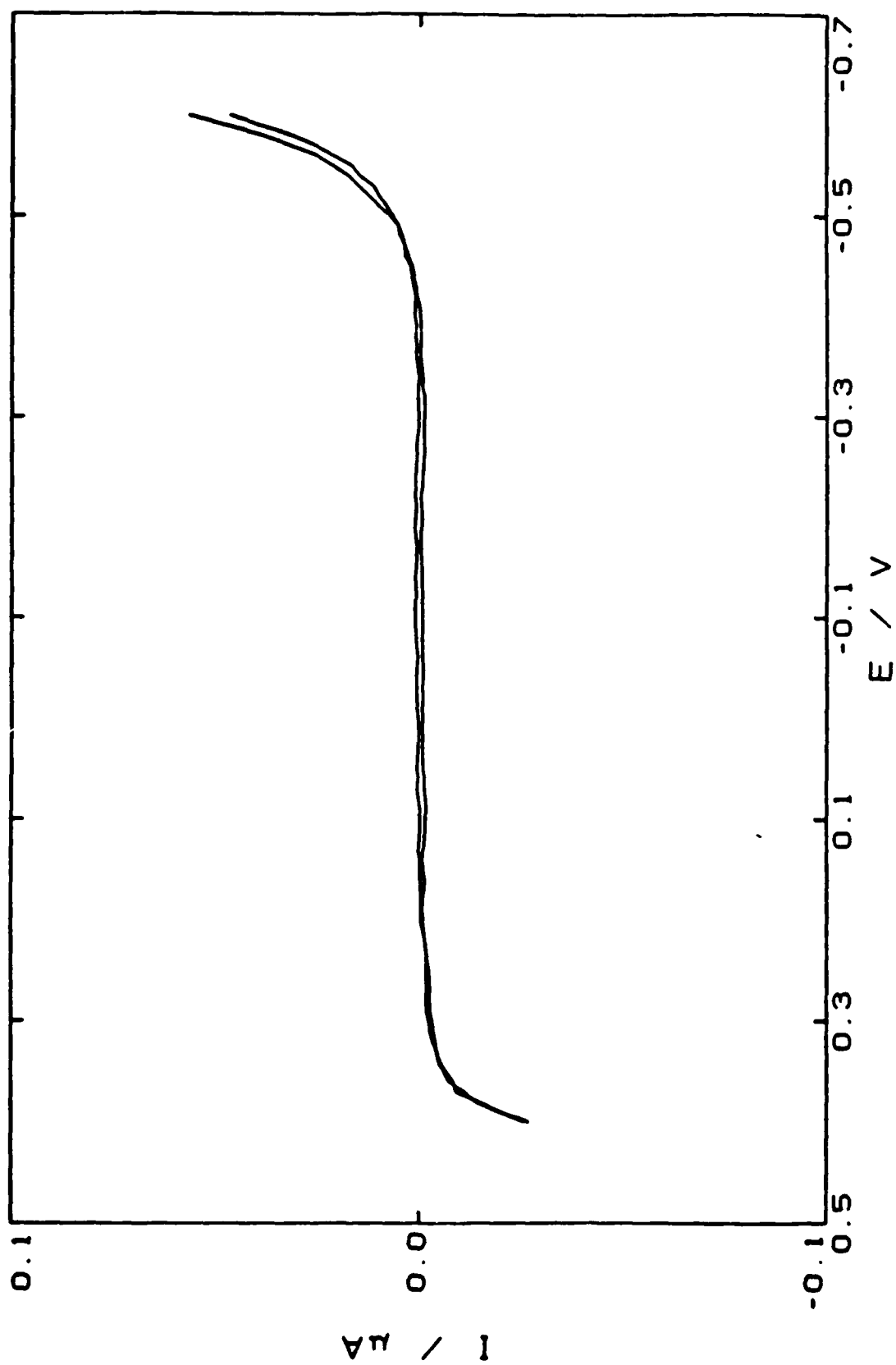


FIGURE 2

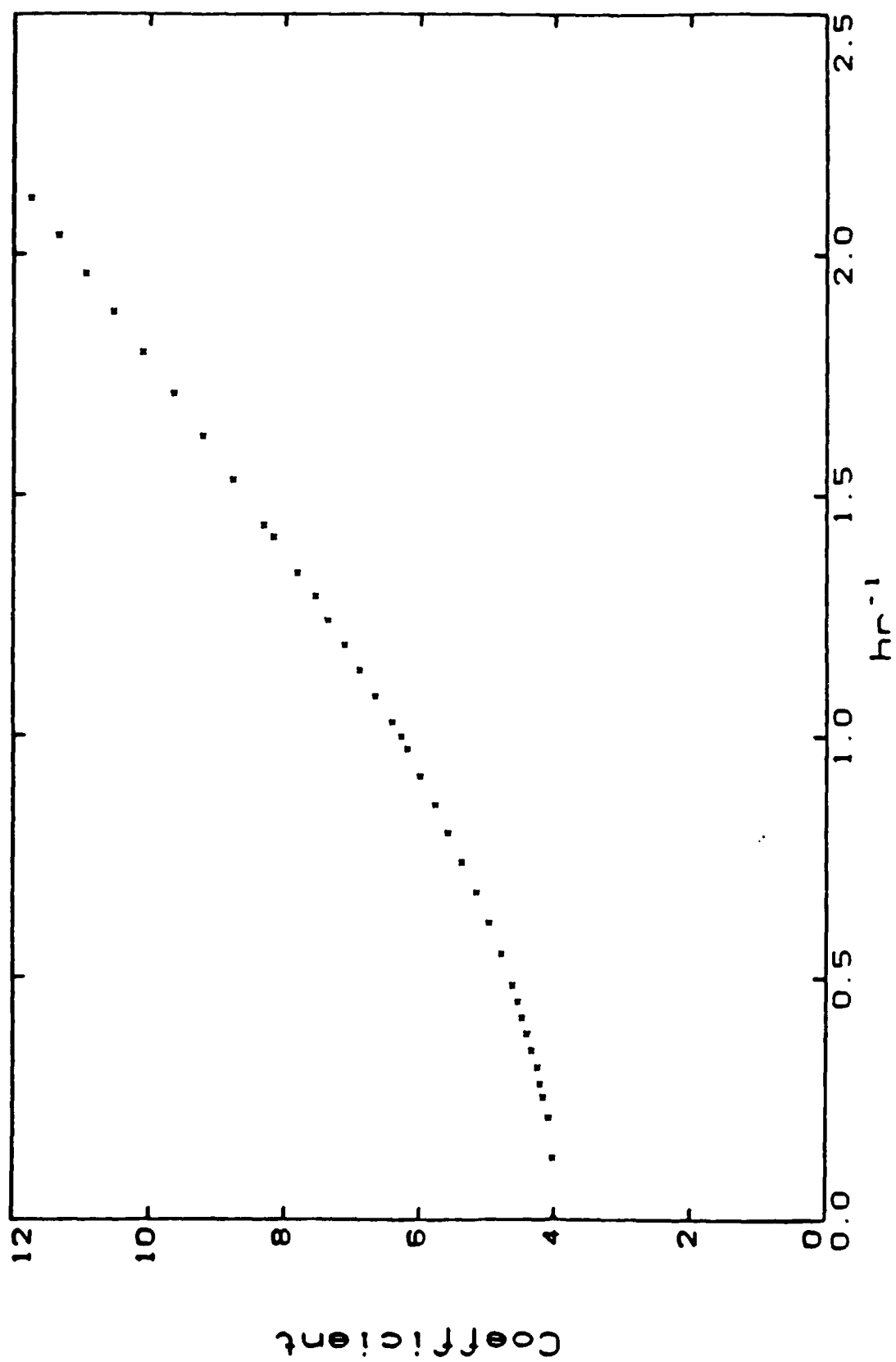


FIGURE 3

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